Implications of Chiral Signatures of PCBs in Soil, Outdoor and Indoor Air in the West Midlands Conurbation, UK

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Introduction

In a previous paper[1], we presented initial results from a study determining chiral signatures of PCBs 95, 136 and 149 in both outdoor air collected using passive air samplers, and topsoil from a number of urban, rural and semi urban locations within the UK's West Midlands conurbation. These limited initial data showed that while chiral signatures in air were essentially racemic, those in topsoil indicated appreciable enantioenrichment of the 2nd eluting enantiomer for PCB 95 and the (+) enantiomer for PCBs 136 and 149. This suggests: (i) that essentially all atmospheric PCBs at all sites arise from racemic (*i.e.* primary) sources, rather than volatilisation from soil; and (ii) that appreciable enantioselective degradation of the monitored PCBs in topsoil occurs.The policy implications of these initial data are significant, as they imply that the principal source of atmospheric PCBs in West Midlands is racemic in nature and is not – as previously widely thought – volatilisation from environmental surfaces (e.g. soil) contaminated with previously deposited PCBs[2].

This paper reports further data from this study, by comparing chiral signatures in outdoor air and soil between October 2003 and September 2004 at the same locations within the West Midlands. As we have previously hypothesised that the ventilation of PCB-contaminated indoor air is the principal source of the racemic PCBs observed in outdoor air[3], we also report here the first measurements of chiral signatures of PCBs in indoor air. In this paper, chiral signatures of PCB #s 136 and 149 are expressed in terms of enantiomeric excess (%ee) expressed as a percentage and defined as:

$$\left| \frac{(\text{the concentration of the } (+) \text{ enantiomer} - \text{the concentration of the } (-) \text{ enantiomer})}{\text{sum of the concentrations of both enantiomers}} \right|$$

In the case of PCB 95, the elution order of the two enantiomers is unknown and %ee values are calculated by substituting the 1st and 2nd eluting enantiomers into the above equation to represent the (+) and (-) enantiomers respectively.

Materials and Methods

Outdoor air and soil samples were collected from 10 sites within the West Midlands conurbation in the UK. Sampling sites were located on a southwest (upwind) to northeast (downwind) transect at intervals of between 3 and 17 km across the conurbation. In this way, a mix of rural (R), suburban (S), and urban (U) sampling locations was studied. Figure 1 shows the location of each outdoor sampling location, with each number relating to a specific location for which data are reported in Table 2. For operational reasons, sampling at location 10 ceased after 2 months and is not reported.

To examine seasonal variability in chiral signatures, one topsoil sample and one air sample per sampling location per month was collected as described previously[3]. Passive air samplers (*i.e.* PUF disks) were employed to provide a time-integrated atmospheric signal over each sampling period at a height of 1.5 m. These have been used successfully in other studies[4, 5]. While their use for determining absolute concentrations requires calibration to determine the air sampling rate of the device, this is unnecessary for the determination of chiral signatures, as only the relative abundance of the two enantiomers is required. Once collected, all samples were stored at 4˚C until extraction and analysis.

Figure 1: Location of Outdoor Sampling Locations

In addition, 20 indoor air samples were collected using PUF disk samplers identical to those deployed to monitor outdoor air. Each sample covers a 1 month period in a different indoor microenvironment within the West Midlands conurbation (not spatially consistent with the outdoor air monitoring locations), with sampling occurring at various points between November 2003 and April 2004.

All samples were extracted, purified, and subjected to enantioselective GC/MS as described previously[3]. We have reported previously the accuracy and reproducibility of our methods for determining chiral signatures of PCBs[1, 3].To evaluate the combined effect of soil sampling and analysis on the precision of our measurements; on one occasion we sampled soil at the EROS location according to our standard procedure, but replicated it so that we had a total of 5 soil samples, which were then extracted and analysed as usual. Table 1 reveals there to be minimal variation in chiral signatures of PCBs 95, 136 and 149 between these soil samples, indicating the extent to which any spatial or temporal differences in chiral signatures observed, are attributable to sampling and/or analytical variability.

Results and Discussion

The average chiral signatures of each measurable target PCB in soil and outdoor air samples at each location for the periods for which data are currently available (11 months for soil and 5 months for air) are presented in Table 2 alongside the average chiral signatures observed for PCBs 95 and 149 in indoor air samples (no data were obtained for PCB 136 as signals were all below our 10:1 signal-to-noise quantification criterion). Table 2 also shows the distance of each outdoor sampling location from the city centre (the Centenary Square monitoring location #7).

Table 2 shows chiral signatures for the three target congeners in soil to be non-racemic at most locations. This confirms earlier findings of enantioselective degradation in soils at concentrations typical of non-industrial locations[1, 3]. As previously reported[1], congener-specific variations in the extent of enantioselective degradation exist. The highest % ee values are observed for PCB 95 (-0.73 to - 11.30 %ee) indicating that this congener is degraded more extensively than 136 (-0.56 to -5.56 % ee) and 149 (0.06 to 5.81 % ee). The direction of this enantioselective degradation of PCB 95 also concurs with earlier work[1, 3] (*i.e.* %ee <0).

One interesting observation is that chiral signatures of PCBs 95, 136 and 149 are essentially racemic in all soil samples taken at the most urban location (# 7, Centenary Square, located in the centre of Birmingham) displaying average % ee values of -0.73, -0.60 and -0.44 for PCBs 95, 136 and 149 respectively. Furthermore, with the exception of the suburban location # 5, the greatest enantioselective degradation of PCB 95 is observed at the most rural locations (sites 1 & 11), with broadly similar – but less conclusive - patterns observed for PCB 136 and 149. These data display obvious agreement with our previous work[6] in soils from the Greater Toronto Area, that indicated an inverse relationship between “urbanisation” (expressed as concentrations of other xenobiotics that could impair microbial activity) and extent of enantioselective degradation of PCB 149 and - to a lesser extent - PCB 136.These racemicchiral signatures at Centenary Square may also reflect the fact that at this highly urbanised location, the rate of racemic atmospheric input to soils may exceed the rate of edaphicenantioselective degradation of PCBs 136 and 149. This could suggest an impact of urbanisation on enantioselective degradation, or it is possible that at highly urbanised locations such as site 7, the rate of racemic atmospheric inputs could exceed the rate of

edaphicenantioselective degradation.

Previously, we had observed indications of temporal (month-to-month) variation in edaphicchiral signatures of a given PCB at the same location[1, 3]. In contrast, an ANOVA test of chiral signatures in soil samples at each location in this study reveals no statistically significant seasonal difference in edaphicchiral signatures.

Table 2 also reveals that chiral signatures in outdoors air for all target PCBs are essentially racemic at all locations. A paired t test analysis of chiral signatures in co-located air and soil samples for the 5 months for which matching sample pairs are available revealed that there are statistically significant differences at sites 1, 5, 6 and 8 ($p<0.05$) for PCB 95 and at sites 3 and 4 for PCB 149. However, there were no significant differences observed for PCB 136 at any site.Although firm conclusions cannot be made until a full year of matching sample pairs are available, this partially complete dataset is largely consistent with our earlier observations[1, 3], implying volatilisation from soil to make a minimal contribution to atmospheric PCB concentrations at each location.

Table 2 also shows that chiral signatures of PCB 95 (and also PCBs 136 and 149, although only 9 samples yielded quantifiable signals for these congeners) in the indoor air samples taken in this study are racemic. The fact that PCB concentrations in indoor air in the West Midlands have been reported previously to exceed those in outdoor air[7] coupled with this evidence of the racemic nature of the chiral signature, adds support to our hypothesis that even today, some 25-30 years after the cessation of PCB manufacture in the UK, it is ventilation of PCB-contaminated indoor air that is the principal source to the urban atmosphere, rather than volatilisation from environmental surfaces such as soil. These results have potentially important implications for public health and environmental protection, as they imply that destruction of PCB stocks remaining in use in indoor environments are likely to result in a significant reduction in atmospheric concentrations. As the atmosphere is the principal point of entry of PCBs into the food chain, and is also the principal vector *via* which PCBs are transported from their – largely urban - source regions, such action is likely to reduce human exposure and limit the future spread of these compounds.

Table 1: Chiral signatures in replicate soil samples from the same location (#6)

Soil #	%ee for PCB 95	%ee for PCB 136	%ee for PCB 149
1	-5.91	-1.33	0.61
2	-6.40	-0.11	0.29
3	-4.35	1.68	-1.01
4	-6.61	3.06	-0.69
5	-6.68	1.71	-1.14
Average	-5.99	1.00	-0.39
RSD (%)	0.97	1.72	0.79

Table 2: Average Enantiomeric Excess Percentage (%ee) values for chiral PCBs obtained for Soil, Outdoor and Indoor Air samples

Sampling Site # from Figure 1 (Classification, Distance (km) from City Centre)	PCB95 Soil	PCB95 Air	PCB136 Soil	PCB136 Air	PCB149 Soil	PCB149 Air
1 (R, 48)	-10.90	-1.58	1.45	-0.46	-0.52	-0.48
2 (R, 31)	-4.52	-1.75	-5.56	-3.10	-2.08	-2.40
3 (R, 21)	-0.73	-2.19	-0.56	1.82	5.81	-1.21
4 (S, 11)	-5.03	-2.21	-0.93	-0.71	0.89	-0.52
5 (S, 6)	-11.30	-1.87	0.86	-0.04	-0.96	-0.73
6 (U, 3)	-5.61	-1.50	-0.62	-0.09	-1.21	-0.52
7 (U, 0)	-0.73	-1.15	-0.60	-0.08	-0.44	-0.22
8 (U, 6)	-9.55	-0.73	-1.15	-1.53	0.06	-2.09
9 (R, 18)	-9.46	-2.20	-1.00	-1.88	2.75	-0.65

11 (R, 31)	-10.11	-1.84	-1.94	-0.37	-1.59	-1.37
Indoor Air	Nq	-1.28	nq	0.54[a]	Nq	0.21[a]

[a]based on nine values only, rest failed detection limit criterion

nd = not detected, failed detection limit criterion; nq = not quantified

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